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The Cellulose-Water Interaction in Rag and Wood Pulps

E. L. Graminski and E. E. Toth

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Polymer Science and Standards Division
Center for Materials Science
National Bureau of Standards
Washington, D.C. 20234

Progress Report Covering the Period
Oct. 1, 1978 through September 30, 1979

February 1980

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I. Summary

The interactions of water with cellulose are of fundamental importance in papermaking and it is essential to know such basic information as how much water is inside the cell wall, how the amount changes throughout the various papermaking stages, and what changes occur in the cell wall structure. It has only been about 10 years since some basic information on the cellulose-water interaction has been acquired, however, the studies have been conducted almost entirely on wood and wood pulps.

The mechanical properties of paper are determined in large part by its microstructure which, in turn, is influenced by the cellulose-water interaction during the pulp preparation stages in papermaking. Rag papers frequently have superior mechanical durability to wood pulp papers and it is possible that the difference in durability between rag and wood pulp papers is derived from differences in microstructure. The development of basic information on the cellulose-water interaction of rag and wood pulps could result in the identification of the parameters affecting the durability of paper. This information would be valuable in the design of durable papers from less expensive, readily available papermaking pulps.

Two different cellulose-water interactions were measured: 1) bound water which is a measure of the accessibility of water to cellulose and 2) the fiber saturation point (FSP) which is the total amount of water within pulp fibers in equilibrium with excess water. Bound water was determined by the non-freezing water technique on a sensitive differential scanning calorimeter. The FSP was determined by the solute exclusion principle using dextran, having a narrow molecular weight range of 2×10^6. The difference between the FSP and bound water was considered to be free or bulk water. The ratio of free to bound water was considered to be a measure of fiber swelling.

Water has a much greater accessibility to wood pulps than to cotton. In addition, the free water to bound water ratio (F/B ratio) is much lower for cotton than for wood pulps indicating a much lower fiber swelling in cotton. On beating, the bound water in wood pulps remains unchanged, but an appreciable increase is observed in cotton. An increase in FSP occurred during beating for all the pulps investigated. The F/B ratio for beaten cotton is considerably lower than the F/B ratio for unbeaten wood pulps. The F/B ratio for fractionated currency machine stock varies with each fraction, being lowest with the longest fiber fraction and highest in the shortest fibers.

The accessibility and affinity of water for cellulose in cotton appears to be much lower than in wood pulps. This implies that interfiber bonding in cotton paper should be much lower than in wood papers. Nevertheless, the mechanical properties of rag papers are frequently superior to those of wood pulp papers suggesting that the mechanical properties are derived from a quite different microstructure. This unique microstructure could be responsible for the excellent durability of currency paper.

Development of basic information on the cellulose-water interaction of wood pulps would be very useful in establishing the criteria for paper durability. In addition, microscopic investigations of rag and wood pulps would assist in the identification of structural differences between rag and wood papers. Such basic information could lead to the design of a paper with less expensive, readily available, paper pulps.

II. Introduction

Pulp fibers are treated mechanically (beating, refining) prior to paper-making in order to obtain paper with a higher density, increased strength, improved formation and a number of other physical properties. During mechanical treatment, a number of changes occur in the pulp fibers which contribute to the modifications of paper properties. Numerous studies, both microscopical as well as physico-chemical, have been conducted to determine just what changes occur in the fibers. Of prime interest are the changes which take place within the cell wall of pulp fibers, however, a lack of experimental techniques has been an obstacle to progress.

It has been theorized that during beating, lateral bonds between neighboring lamellae in the cell wall are broken allowing water to enter, enabling the lamellae to slide past one another and results in increased fiber flexibility (1). Evidence that some such process occurs is considered to be substantiated by the fact that during beating, pulp fibers become more flexible, collapse more easily, and disintegrate into sheet-like films or debris. Unfortunately, details of the process are lacking. There is great difficulty in examining the interior of the cellulose-water gel in the presence of water and in the ability to follow the structural changes during mechanical treatment.

Most methods for examining the structure of a porous system are applicable only to dry materials. Consequently, fibers were dried by freeze-drying and by solvent-exchange in order to obtain dry fibers with the same porous structure as in the water-swollen state. When it was found that the swollen structure of pulps was only partially preserved by either of the drying methods (2), a search was made for new methods of investigating the water swollen structure of pulps in the presence of water.

One method was developed for determining pore size distribution in wet fibers which evolved from earlier work on "nonsolvent water" (3). The technique was termed "solute exclusion". The "solute exclusion principle" consists of equilibrating a sample of wet pulp containing a known quantity of water with an aqueous solution of polymeric molecules of known hydrodynamic size and known concentration. The solute molecules then diffuse into all the water associated with the fibers except for the water contained in pores of narrower widths than the solute molecules. The solution becomes more dilute but only to the extent that the solute molecules can diffuse. From the resultant change in concentration it is possible to calculate the amount of inaccessible water.

If the polymeric solute material is high in molecular weight and the hydrodynamic molecular size exceeds the largest pore size of the fibers, then the total amount of water contained in the fibers can be calculated. For all intent and purposes dextran, of molecular weight 2×10^6, has the appropriate molecular size to meet the requirements to be totally excluded from the fiber pores. Furthermore, dextran is available in a narrow range of molecular weight fractions. The total amount of water, within pulp fibers in equilibrium with excess water, is known as the fiber saturation point (FSP).

Part of the water within moist cellulose fibers exhibits properties which are markedly different from those of the rest of the water and is referred to as bound water. Apparently bound water is attached to the surfaces of cellulose by hydrogen bonding and consists of one or more layers of water. The structure and thermodynamic properties of bound water are significantly different from free or bulk water. While its existence has been recognized for some time, quantitative measurement of bound water has led to disagreement as to its exact quantity in various materials. Numerous methods have been used to determine

bound water in cellulose such as solute exclusion, non-solvent water, non-freezing water, rate of cooling, rate of drying, heat of melting, desorption isotherm analysis and more recently nuclear magnetic resonance. The quantity of bound water determined appears to be dependent on the measurement method.

The variance in the amount of bound water determined by various methods should not be surprising as it is likely that the thermodynamic behavior of bound water molecules includes a wide range of physical properties. There simply aren't two sharp, well-defined, homogeneous phases of water in the cellulose-water system each with its own set of unique physical properties. NMR relaxation studies demonstrate this point clearly since no sharp boundary exists between bound and free water[14]. The response of the various molecules of bound water to different measurement techniques will not be alike and as a consequence, the amount of bound water measured by each technique will vary.

The amount of bound water depends on the accessibility of cellulose to water. The accessible regions are the amorphous fraction, the partially crystalline material and the surfaces of the perfectly crystalline fraction. In wood pulp, hemi-cellulosic materials are also accessible to water but the exact manner in which it interacts with water is unknown.

Determination of bound water and the fiber saturation point would be very useful in studies on the beating of pulps. Increases in the fiber saturation point are presumably due to fiber swelling but the exact mechanism for fiber swelling is unknown. An increase in the FSP is caused either by a decrease in crystallinity or simply by an expansion of the lamella. If the increase in FSP is the result of decreased crystallinity, new surfaces would be generated and the amount of bound water would increase. If the increase was due to an expansion of the lamella, no change in bound water would be expected

The procedure for determining the fiber saturation point has been developed adequately and is discussed extensively in a recent publication by Scallan (4). No acceptable method has been developed for determining bound water although attempts have recently been made by NMR (5,6) and by differential scanning calorimetry (7-9). For all intent and purposes, the methods are empirical in nature as they involve numerous assumptions. Of the two methods, the microcalorimetric method appeared to be the more useful because of the relative simplicity of the method and ease of sample preparation. A common failing with the microcalorimetric methods was the uncertaintly of the exact amount of water and anhydrous fibers in each specimen. It was assumed that each specimen had the same ratio of fiber and water as the bulk sample.

The purpose of this investigation was to develop a microcalorimetric method for the quantitative determination of bound water and to determine the effect of beating on bound water in wood and rag pulps.

III. Experimental Details

A. Fiber Saturation Point

A stock solution of dextran (M.W. 2×10^6) at a concentration of 20.000 g/dm^3 was prepared as follows. The solute (20.000 g) was dissolved in approximately 500 cm^3 distilled water at the boil. The solution was cooled to ambient temperature and then transferred quantitatively to a liter volumetric flask. Additional distilled water was added, sufficient to make a liter of solution. The dextran solution was then filtered through a medium glass frit filter into a screw cap polyethylene bottle and stored in a refrigerator.

A calibration curve for the dextran solution was prepared by diluting weighed amounts of the stock solution (approximately 20 g) with 0-5 grams of distilled water. Ten different solutions were prepared. The optical rotation of these solutions was measured on a sensitive polarimeter capable of measuring the optical rotation to the nearest five thousandth of a degree. A plot of grams dextran/gram solution against the degree of rotation was prepared.

Pulp samples, approximately 50 g, were soaked in one liter of distilled water for one hour, then filtered through a coarse glass frit. After being washed according to this procedure three times, the pulp was soaked for a minimum of 18 hours in distilled water. The following day the pulp suspension was filtered, divided into eight specimens of approximately equal weight (6-7 g) and weighed on an analytical balance to the nearest tenth of a millagram in a screw cap polyethylene bottle having a 50 cm^3 capacity. Approximately 20 g of the stock solution of dextran, weighed on an analytical balance to the nearest tenth of a milligram was added to each bottle. The bottle caps were screwed on firmly and attached to a wrist action shaker and agitated for a minimum of 18 hours. The following day the liquid was decanted from the specimen into a clean, dry centrifuge tube and the excess liquid in the pulp mass was removed by pressing the mass with a spatula. The centrifuge tube was stoppered and centrifuged at 1000 g's until the liquid appeared completely clear (approx. 15-30 minutes). After centrifugation the clear supernatant liquid was decanted into a clean, dry, 30 cm^3 glass stoppered flask.

The solid residue in the centrifuge tube and the pulp mass in the polyethylene bottle were transferred quantitatively to a one liter beaker and suspended in approximately 500 cm^3 distilled water for 3-4 hours. The suspension was then filtered through a previously weighed coarse glass filter and the fibrous mass was washed several times with fresh distilled water. The glass filters were then dried in a vacuum oven at 105 °C for one hour, placed in desiccators to cool and weighed to determine the amount of anhydrous pulp in each specimen.

After centrifugation, the optical rotation of the clear, supernatant dextran solution was measured on the precision polarimeter. Before the polarimeter cell was filled for the optical rotation measurement, the cell was rinsed twice with several cm^3 of the solution to be measured then filled with the solution. The cell was placed in the polarimeter and five minutes were allowed for the temperature of the solution to come into equilibrium with the cell, thermostated at 20°C. The optical rotation was then measured six to ten times at one minute intervals and the average of the readings was considered to be the optical rotation of the solution. The concentration of the solution was determined from the calibration curve and the amount of water diluting the stock solution calculated as follows

$$W_D = \left(\frac{gi}{gf} - 1\right) \times p$$

where

W_D = weight of water diluting stock dextran solution
g_i = concentration of stock dextran solution
g_f = concentration of diluted dextran solution
p = weight of stock dextran solution

The fiber saturation point was then determined as follows

$$FSP = \frac{(W_T - W_D)}{f_d}$$

where

W_T = grams of water in specimen
W_D = grams of water diluting stock dextran solution
f_d = grams of dry fibers in specimen

B. Determination of Bound Water

Samples of unbeaten and beaten pulp were washed three times by soaking in distilled water for one hour and decanting the supernatant liquid. After the final wash the excess water was removed by pressing the pulp mass with a spatula. The sample was then soaked for at least 18 hours in excess distilled water. The following day the water was removed by decantation and the excess water removed once again by pressing the wet pulp mass with a clean spatula.

Approximately 3-6 mg of wet pulp was placed in previously weighed aluminum sample holders and sealed hermetically. The sample holders and covers were dried at 105°C for one hour in a vacuum oven and cooled to ambient temperature before weighing on a microbalance. The sealed sample holders were then weighed on a microbalance to the nearest microgram. Before the sealed specimens were placed in the differential scanning calorimeter (DSC) on the following day they were weighed on a microbalance once again. If the second weight changed by more than 2-3 µg, the sample holder was considered improperly sealed and was discarded.

The sealed samples were placed in the sample holder of the DSC and allowed to stand for five minutes before cooling to 240°K. The cooling rate was 5°/min. Following cooling, the samples were heated at 5°C/min. up to 290°K. The cooling and heating procedure was repeated a second time for each specimen. Following measurement on the DSC each specimen was weighed once again. If the weight did not change by more than 2-3 µg, the specimen was considered to be adequately sealed, otherwise the sample was discarded. If the specimen was sealed satisfactorily, the cover of the specimen holder was pierced with a sharp mandrel and dried in a vacuum oven at 105°C for one hour, cooled to ambient temperature in a desiccator and weighed on a microbalance. As cellulose is hygroscopic, and as the specimen was exposed to the atmosphere, the weight of the specimen and holder was measured every 15 seconds for three minutes. A plot of weight as a function of time was prepared and extrapolated to zero time to estimate the true anhydrous weight of the specimen. After a considerable number of specimens were weighed in this manner, it was recognized that the weight obtained within the first 30 seconds was within one microgram of the extrapolated weight. The specimen was redried, cooled and weighed repeatedly until the difference between consecutive weighings was no greater than 2-3 µg.

The DSC was calibrated with weighed specimens of distilled water. The water specimens were cooled to 240°K at 5°C/min then heated to 290°K at 5°C/min. The area under the melting curve was determined with a planimeter as suggested by Flynn (10). Using the value of 79.71 cal/g as the heat of fusion for ice, a

calibration constant was calculated. The amount of ice formed in each pulp specimen was calculated from the area under the curve and the calibration constant. The difference between the total weight of water in the specimen and the weight of ice formed was defined to be the amount of water bound to the cellulose.

C. Pulp Samples

Two kraft wood pulps and a virgin cotton were investigated. The wood pulps were prepared from single logs of Norway Spruce and Slash Pine. The Norway Spruce was pulped to a yield of 47.5% and a Kappa No. of 41.8. The Slash Pine was pulped to a yield of 44.9% and had a Kappa No. of 45.7. The purified cotton sample was received from the Southern Regional Research Center and was obtained from the Mississippi Delta region (Delta Pine, smooth leaf variety). The cotton was purified by a modification of the Conrad method (11) with the addition of an 8 hour boil in 1% NaOH under N_2 atmosphere, washed successively with distilled water, 1% acetic acid, 1% NH_4OH and finally distilled water. It was then dried in a vacuum oven at 60°C. All of the specimens were placed in polyethylene bags, inserted in metal cans which were sealed and stored in a freezer. The wood pulp samples were never dried.

Beating was done in a laboratory mill at a 10% consistency with distilled water for 5000 revolutions at a relative velocity of roll to bedplate of 6 m/sec at a force of 3.4 kilograms.

Currency stock was obtained from Crane and Company, Inc. The stock was obtained after the beater, but before passing through the refiners and jordan. The consistency of the currency stock was approximately 1-2% when received. Excess water was removed by filtration on a large Buchner funnel. After filtration, the consistency was approximately 25%.

IV. Results and Discussion

The legitimacy of determining the FSP and bound water is dependent on the accuracy of several assumptions. In determining the FSP, it is assumed that the hydrodynamic diameter of dextran, molecular weight 2×10^6, is greater than the diameter of most of the pores in swollen cellulose. Furthermore, it is implied that water, bound to the surface of cellulose and in contact with the dextran solution, behaves as free water and will take part in the dilution of the dextran solution. The validity of the latter assumption has never been proven. If water, bound to the surfaces of pulp fibers, does not participate in the dilution of dextran, the errors in calculating FSP would be expected to be small except in cases where the surface area is high. The determination of FSP for very fine cellulosic material as fines and debris or of highly fibrillated fibers could lead to spuriously high results.

In determining bound water by the nonfreezing water technique it is assumed that only bound water does not freeze and that the heat of fusion of the frozen water is identical to that of bulk water. It is likely that the nonfrozen water not only involves water firmly bound to cellulose, but also loosely bound water and water whose structure is affected by surfaces, as in very fine capillaries. The free water in fibers is the difference between the FSP and the bound water.

Two factors, 1) drying of the sample holders, and 2) the quantitative determination of the water and dry fibers in each specimen, were important in measuring bound water. If the sample holders were not previously dried both the mean and standard deviation were affected as shown in Table 1. If the quantity of water in each specimen was assumed to be identical to the bulk of the sample, the standard deviation was affected as shown in Table 2.

The bound water content of cotton is approximately one half that found in both wood pulps. It is quite obvious that bound water is a function of accessibility and not crystallinity. Two cellulosic materials, with an identical amount of amorphous material, but different crystal size, would have different amounts of bound water. As the crystal size and/or the crystal perfection decreases the number of hydroxyls lying at the surface, increases. Therefore, increasing the crystal surface to volume ratio increases the amount of bound water.

The FSP for wood pulps is approximately 2.5 times greater than it is for cotton. Not only is cotton less accessible to water, it cannot accommodate free water as does wood pulp. This is indicated very well by the free water to bound water (F/B) ratio. The F/B ratio for wood pulp is approximately 1.5 times greater than it is for cotton.

Beating has no effect on the bound water content of wood pulp, but a substantial increase is observed in beaten cotton. Presumably, new surfaces are generated during beating. The manner by which the new surfaces are generated is not known, but cotton does fibrillate readily during beating and large amounts of debris are formed. In any event, the disparity in bound water between wood pulp and cotton decreases during beating.

Increases in FSP occur during beating for both wood pulp and cotton. Even though the percent increase in FSP is larger in cotton than in the wood pulps, the increase in the F/B ratio is much greater in wood pulp than in cotton. This indicates that cotton does not swell as much as does wood pulp during beating. In fact, the F/B ratio for beaten cotton is lower than the F/B ratio for unbeaten wood pulp. Apparently, the lamella in cotton do not separate as much as they do in wood pulps.

Since cotton swells less than wood pulp during beating, the cotton fibers should be less flexible and should not form interfiber bonds as readily as wood pulps. The strength, durability, and other mechanical properties, dependent on interfiber bonding, ought to be superior in wood pulp papers. However, high grade rag papers such as currency paper, have superior strength and mechanical durability to that found in high quality wood pulp papers. Since high quality rag papers are strong and durable, indicating the presence of strong bonding, it must be assumed that the mechanical properties of rag papers are derived from a microstructure quite different from that found in wood pulp papers.

The bound water, FSP, and F/B ratio varied for each of the four different fiber length fractions, being lowest for the longest fiber fraction and highest for the shortest fiber fraction. It was interesting to note that the F/B ratio of the longest fiber fraction was identical to that found in unbeaten cotton. Apparently, the long fibers do not swell when beaten. As mentioned previously, a large amount of debris is generated during beating. This debris probably has a much larger surface area than the long fiber fraction. It would be of interest to determine whether the surface area of the fines is responsible for the increased bound water and FSP.

In a previous study on fractionated wood pulps (11) it was found that the FSP for similar fractions was lower than for the unfractionated pulp, but that the FSP for the material passing through a 100 mesh screen was considerably higher (3.9 to 5.8gH_2O/g. fiber). In this study, the finest screen used was 150 mesh and since the material passing through that screen was not recovered, the FSP could only be estimated (Fraction V). There is a very great difference between the determined FSP of the fines in wood pulp and the calculated FSP for the fines in currency stock. However, it is not known whether the apparent cellulose-water interaction of the fine material differs depending on whether it is combined with the whole pulp or separated from it. It will be necessary to check this point further.

Previous studies on fractionated currency stock (12) and on fractionated wood pulps (13) indicate that bonding in handsheets, made from individual fractions, is much greater in wood pulp than in currency stock. Furthermore, the difference in the strength of handsheets, made from the unfractionated pulp and those made from the individual fractions is quite high for currency stock but minimal for wood pulp, indicating that the bonding mechanism in wood pulp is similar in all the fiber length fractions, but not in currency stock. Evidently, the manner by which currency paper derives its mechanical properties is very different from the manner wood pulp properties are derived. This suggests two entirely different microstructures are operative.

V. Conclusions

The cellulose-water interaction in rag pulps is considerably different from that in wood pulps. Apparently, the long fiber fractions of rag pulp do not swell as extensively as do wood pulps and consequently, do not form many or very strong interfiber bonds. The excellent mechanical properties of rag paper must originate with a microstructure considerably different from that in wood pulps. Additional data on the cellulose-water interaction in the various fractions of currency machine stock will be necessary in order to determine more fully the specific differences in wood and rag pulp papers.

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Table 1. The Effect of Sample Holder Drying on the Determination of Bound Water in Slash Pine Pulp

Specimen Number	Bound Water $g.H_2O/g.$ fiber	
	Undried Sample Holders	Dried Sample Holders
1	.502	.477
2	.360	.421
3	.418	.437
4	.435	.409
5	.386	.425
6	.366	.455
7	--	.424
Mean	.411	.431
Standard Deviation	.053	.016

Table 2. The Effect of Determining the Water in Each Specimen on the Estimation of Bound Water in Norway Spruce Pulp

Specimen Number	Bound Water $g.H_2O/g.$ fiber	
	Based on Total Water in Sample	Based on Total Water in Each Specimen
1	.428	.507
2	.387	.442
3	.367	.436
4	.444	.427
5	.529	.481
6	.556	.446
7	.458	.434
Mean	.453	.453
Standard Deviation	.069	.030

Table 3. The Fiber Saturation Point and Bound Water of Two Kraft Wood Pulps and Purified Cotton

	Norway Spruce		Slash Pine		Purified Cotton	
	Unbeaten	Beaten	Unbeaten	Beaten	Unbeaten	Beaten
			Fiber Saturation Point			
g H_2O/g fiber	1.326	1.785	1.294	1.867	0.530	0.936
standard deviation	0.037	0.020	0.036	0.052	0.058	0.047
no. of specimens	8	7	8	6	3	7
			Bound Water			
g H_2O/g fiber	0.453	0.449	0.431	0.433	0.234	0.342
standard deviation	0.030	0.057	0.016	0.049	0.034	0.012
no. of specimens	7	7	7	9	7	7
			Free Water			
free water g H_2O/g fiber	0.873	1.336	0.863	1.434	0.296	0.594
Free Water / Bound Water	1.9	3.0	2.0	3.3	1.3	1.7

Table 4. The Fiber Saturation Point and Bound Water for Fractionated Currency Stock

Fraction	I	II	III	IV	V	Unfractionated
			Fiber Saturation Point			
g H_2O/g fiber	0.800	0.831	1.032	1.355	1.430*	1.032
standard deviation	0.020	0.017	0.037	0.012	--	0.027
no. of specimens	7	7	7	7	--	6
			Bound Water			
g H_2O/g fiber	0.353	0.387	0.383	0.403	--	0.388
standard deviation	0.015	0.025	0.021	0.028	--	0.028
no. of specimens	10	10	10	10	--	10
			Free Water			
free water g H_2O/g fiber	0.447	0.544	0.649	0.952	--	0.644
$\frac{\text{Free Water}}{\text{Bound Water}}$	1.3	1.4	1.7	2.4	--	1.7

*Estimated

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☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

The interaction of water with cellulose has been determined for two wood pulps, a purified cotton and for currency paper machine stock. Two different interactions were measured, 1) bound water which measures accessibility of cellulose to water and 2) the fiber saturation point which measures the total amount of water within cellulose fibers. Bound water was determined by the non-freezing water technique and the fiber saturation point was determined by the solute exclusion principle. Wood pulp is more accessible to water than is cotton. Beating does not increase accessibility to water in wood pulps but it does increase in cotton signifying the generation of new surfaces in cotton. Wood pulps swell more extensively on beating than does cotton. Most of the water interacting with cellulose in currency machine stock is in the short fiber fraction. There appears to be considerable difference in the interaction of water with the fines in beaten wood pulp and in beaten cotton.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Bound water; fiber saturation point; fiber swelling; paper microstructure; paper durability; interfiber bonding; cellulose accessibility.

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